containing a few drops of water at reflux for 12 hours. Dilution with 250 ml. of water yielded a small recovery of the amide (0.21 g.), and acidification and cooling of the filtrate gave after purification 0.80 g. (40%) of yellow needles, m.p. 201–204°; mixed melting point with an authentic sample of ferrocenoic acid (m.p. 210° dec.), 204–206°.

1-Acetyl-1′-carbamylferrocene was prepared by a procedure essentially identical to that described above for 1-acetyl-1′-diphenylcarbamylferrocene. From 4.6 g. (20 millimoles) of carbamylferrocene was obtained 3.2 g. (61%) of the acetylcarbamylferrocene as orange-red crystals (from benzene) melting at 151–152°.

Attempted hydrolysis of 1-acetyl-1′-carbamylferrocene in 10–15% ethanolic potash, acetic–hydrochloric acid mixtures, concentrated hydrochloric acid, and sulfuric acid containing sodium nitrite gave only intractable tars.

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The Constitution of Organoberyllium Halides

BY RAYMOND E. DESSY

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Exchange in the system $(C_6H_5)_2Be \cdot Be^*Br_2 \rightleftarrows (C_6H_5)_2Be + Be^*Br_2 \rightleftarrows 2C_6H_5Be^*Br$ has been investigated using Be^7 as a tag. Results show that there is no exchange of Be between the two species $(C_6H_5)_2Be$ and $BeBr_2$, and indicate that there is no such structure as C_6H_5BeBr.

It has been made increasingly clear, over the last few years, that equilibria of the Schlenk type

$$R_2M + MX_2 \rightleftarrows 2RMX \qquad (1)$$

used to represent the structure in solution of organometallic compounds of the Group II metals are not universal. By use of radioactive tracers it has been shown[1] that where M = Mg, and R = Et, C_6H_5, there is no exchange of Mg between R_2Mg species and Mg^*X_2 species, thus indicating the non-existence of RMgX. Similarly, Garrett[2] has reported that where M = Cd and R = Et there is no evidence for exchange of Cd between R_2Cd species and CdX_2 species.

The existence of the species $R_2Cd \cdot CdX_2$ receives support from equilibrium constant measurements and molecular weight determinations. Preliminary data[2] involving measurements of equilibrium constants in the system M = Zn and R = Et also indicate the non-existence of the RZnX species.

On the other hand, there is little doubt that in the system M = Hg, and R = alkyl, aryl that a species such as RHgX does exist—it is isolable, and molecular weights indicate a monomer. In most solvents the equilibrium appears to be almost quantitatively to the right. Rate measurements have been made on the system, and a mechanism for the reaction has been proposed.[3,4]

It thus appears that there is only one demonstrable case of the existence of an RMX compound. Beryllium seemed to provide the most important additional test case.

The normal reaction between an alkyl halide and beryllium metal apparently cannot be used to form an organoberyllium halide.[5] Gilman has succeeded[6] in preparing ether solutions of substances described as organoberyllium halides by reaction of RX compounds and Be metal in the presence of $HgCl_2$ as a catalyst under high pressure and temperature. No analytical data were reported.

Gilman also has pointed out[7] that solutions of dialkylberyllium react with an excess of beryllium chloride to give a solution "with the characteristics" of "organoberyllium halides." Apparently all that is known about the differential behavior of dialkylberyllium compounds and "organoberyllium halides" is that the former react more rapidly with Michler ketone.[8] It also has been shown[8] that thermal decomposition of the materials termed organoberyllium halides leads to the formation and evolution of dialkylberyllium compounds. All of this evidence for the existence of RBeX is speculative.

Coates[9] reports that although $(CH_3)_2Be$ reacts with methanol explosively, the reaction with HCl requires long periods of heating. The gas evolved was identified as methane, and the white solid remaining was assumed to be methylberyllium chloride ($\log P_{mm} = 6.52 - 2614/T$; *cf.* $(CH_3)_2Be$ where $\log P_{mm} = 13.29 - 5100/T$).

In light of the scant knowledge as to the existence of organoberyllium halides, it was felt that an investigation of exchange in the system

$$R_2Be \cdot Be^*X_2 \rightleftarrows R_2Be + Be^*X_2 \rightleftarrows 2RBe^*X \qquad (2)$$

would be of value. For practical reasons, R was chosen to be phenyl and X bromine.

Experimental

Beryllium Metal.[10]—Cyclotron target material having the analysis (spectrographic) given was used: Al,

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(1) Raymond E. Dessy and G. S. Handler, THIS JOURNAL, **80**, 5824 (1958).

(2) A. B. Garrett, Arthur Sweet, W. L. Marshall, David Riley and Anis Touma, *Rec. Chem. Progress*, 155 (1952).

(3) Raymond E. Dessy and Y. K. Lee, THIS JOURNAL, **82**, 689 (1960).

(4) In a paper by I. B. Johns and R. M Hixon (*J. Phys. Chem.*, **34**, 2226 (1930)) in which measurements of the equilibrium constant for the above reaction were measured by e.m.f. studies on the cell

$$\text{Hg} \mid \begin{array}{l} HgI_2\ 0.005\ M \\ KI\ 0.05 M \\ EtOH \end{array} \parallel \begin{array}{l} R_2Hg + HgI_2 \rightleftarrows 2RHgI \\ KI\ 0.05\ M \\ EtOH \end{array} \mid \text{Hg}$$

it was concluded that in the series R = Me, Et, *n*-Bu the equilibrium constant was of the order of 100, but when R = C_6H_5 of the order of 1. It seems apparent that their assumptions that the junctions RHgI/Hg and R_2Hg/Hg are zero are invalid. Although the experimental technique looks promising, further work apparently is necessary.

(5) Henry Gilman, THIS JOURNAL, **45**, 2693 (1923).

(6) Henry Gilman and F. Schulze, *ibid.*, **49**, 2904 (1927).

(7) Henry Gilman and F. Schulze, *J. Chem. Soc.*, 2663 (1927).

(8) Henry Gilman and F. Schulze, THIS JOURNAL, **49**, 2904 (1927).

(9) G. E. Coates, F. Glockling and N. D. Huck, *J. Chem. Soc.*, 4512 (1952).

(10) All handling of beryllium metal should follow the suggestions laid down in the pamphlet "Some Notes on Safe Handling Practices for Beryllium," distributed by the Defense Metals Information Center, Battelle Memorial Institute.

0.05; Cr, 0.03; Cu, 0.001; Fe, 0.05; Ca, 0.03; Ge, 0.005; K, 0.05; Li, 0.01; Mg, 0.01; and Mn, Ni, and Si, <0.01%. The brick metal was machined down to ten-thousandths inch chips for further reactions.

Beryllium bromide was prepared by the reaction of beryllium metal with bromine (Mallinckrodt A. R.) in ether and the solution filtered through a medium porosity frit. The reaction is rapid, and a two-phase system results, similar to that observed in the Mg series. The darker lower layer is beryllium bromide etherate, with some dissolved ether, m.p. *ca.* 25°; while the upper layer is beryllium bromide etherate dissolved in ether. The lower layer was analyzed for halogen by potentiometric titration with silver nitrate. It was found to be 5.78 *M* in bromide ion and therefore 2.89 *M* in $BeBr_2$. The material is sensitive to light and moisture, darkening rapidly upon standing, and hydrolyzing in air with evolution of HBr. It was prepared shortly before use, and stored in sealed glass ampoules.

Diphenylberyllium was prepared by a modification of the procedure proposed by Wittig.[11] Beryllium metal (1.0 g., 0.11 mole) and diphenylmercury (10 g., 0.028 mole) were placed in a Carius tube along with 0.5 g. of $HgCl_2$ and 0.5 g. of anhydrous $BeBr_2$ dissolved in 1 ml. of ether. The tube was evacuated, sealed, and heated to 170° for 72 hours. At the end of this time the beryllium metal was thoroughly amalgamated, and drops of mercury were evident.

The ampoule was opened in a dry-box filled with nitrogen, the contents extracted with boiling dry xylene, and the hot extract filtered through a medium sintered glass plug to remove finely suspended solids. Part of the solvent was removed, and the solution cooled to −60°. The resulting solid was filtered off using a medium frit, and washed with cold xylene. It was washed off the frit with ether (caution: heat evolution) and stored as the etherate solution in a glass ampoule with a stopcock equipped with a hypodermic adapter. The solution gave a very positive, rapid Gilman Color Test, with Michler ketone, a negative mercury test, using $SnCl_2$, and showed less than 4 mole-% halogen; 1-ml. aliquots were hydrolyzed with NH_4OH, and ashed to BeO at 700°. On the basis of the weight of BeO obtained, the solution was 0.58 *M* in diphenylberyllium.

Solvents.—The ether was Matheson, Coleman and Bell absolute anhydrous and was stored over sodium wire. The dioxane was purified by distillation from ethyl Grignard, and was stored in sealed ampoules.

Transfers.—All transfers were accomplished in a dry-box nitrogen atmosphere, using hypodermic techniques. Contamination with oxygen was rigorously avoided.

Radioactive Beryllium Bromide.—A 0.5-g. Li^7 target was bombarded in the Ohio State University Cyclotron at 6 Mev. at 9 μa. for 8 hr. [$Li^7(p,n)Be^7$]. The target was dissolved in 30 ml. of water containing 100 mg. of $BeBr_2$ carrier. This was acidified with 10% HCl and filtered through a medium porosity frit to remove suspended solid. The resulting clear solution had considerable activity. It was made basic (*p*H 11) with 10% NH_4OH, and white colloidal $Be(OH)_2$ was noted. This was allowed to coagulate for two hours, and then the suspension was filtered through a sintered glass bed with 5-μ pores. The activity remained on the frit, and was washed with two 1-ml. portions of water. The $Be(OH)_2$ was washed off the filter with 1 ml. of 10% HCl. The water was removed from this solution, 1 ml. of $SOCl_2$ was added, and the material heated to reflux for 10 minutes. The $SOCl_2$ then was distilled off and the tube temperature raised to 200° for 5 minutes to remove traces of acid; 2 ml. of $BeBr_2$ dietherate was added to give the tagged $BeBr_2$ solution. A slight layer of ether was added to maintain the two-phase system in equilibrium.

Exchange Run.—Diphenylberyllium in ether (14.5 mmoles) and tagged beryllium bromide in ether (14.5 mmoles) were mixed with sufficient ether to yield a solution 0.25 *M* in each. This was permitted to stand for 15 minutes, and then 0.6 ml. of dioxane was added over a 15-minute period. Dry runs indicated that a large excess of dioxane and slow addition are required for good precipitation of beryllium bromide. After a 30-minute waiting period the clear supernatant was withdrawn, and an aliquot hydrolyzed with NH_4OH, ashed to BeO, and counted. Potentiometric halogen analysis indicated 0.08 *M* total halogen. The solution was 0.25 *M* in Be.

A sample of the original tagged beryllium bromide was also hydrolyzed and ashed to BeO, and counted.

Counting.—Be^7 decays by K capture, with a $t_{1/2}$ of 54 days. Counting and identification were done on a 100 Channel R.I.D.L. Analyzer using a 4″ × 4″ solid sodium iodide (thallium activated) crystal and a 6364 Dumont tube. Channel width was 20 Kev. All counting is corrected for dead time and background. The samples were all BeO, of approximately equivalent weight, and geometry. All of them showed a large spike around 0.48 Mev.[12]

Any contaminants present had intensities of less than 0.1% of the main peak.

For comparison, the integrated count covering the range 0.44–0.52 Mev. was used. This eliminates any error that might arise from shifts in the apparent energy of the peak at high intensities.

Results and Discussion

Table I shows the results obtained by attempting beryllium exchange between $(C_6H_5)_3Be$ and Be^*Br_2 in ether using Be^7 as a tag. The beryllium bromide and diphenylberyllium dissolved in ether were mixed to give a solution 0.25 *M* in each component and permitted to stand for 15 minutes. Sufficient dioxane was added to cause the almost complete precipitation of the beryllium bromide present. The supernatant was withdrawn, and an aliquot hydrolyzed and ashed to BeO for counting. At the same time an aliquot of the original beryllium bromide was hydrolyzed and ashed to BeO for counting.

TABLE I

Sample		Sample wt. (as BeO), mg.	c./m.,− BCKD. (0.44–0.52 Mev.)	Specific activity, c./m.-mg. BeO	Activity ratio
Original Be^*Br_2		17.9	154,704	8,640	1.00
$(C_6H_5)_2$-Be^a	Uncorr.	11.4	15,212	1,335	0.15
	Cor.	...	...	0	0

[a] Analysis indicated the supernatant material remaining after dioxane precipitation was 0.25 *M* in Be, 0.08 *M* in halogen. Therefore, 16% of the Be arose from unprecipitated Be^*X_2, and 84% from $(C_6H_5)_2Be$. The amount of activity such contamination would contribute, assuming no exchange, is equal to the observed specific activity in the supernatant, within experimental error.

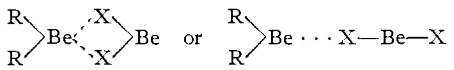
If a species such as C_6H_5BeBr did exist in equilibrium with the starting materials statistical exchange would have been observed, with a ratio of 1:0.5 between the specific activities.

$$(C_6H_5)_2Be + Be^*Br_2 \rightleftharpoons 2C_6H_5Be^*Br \qquad (3)$$

It is obvious that such is not the case, and this indicates *there is no such species as C_6H_5BeBr* in equilibrium with $(C_6H_5)_2Be$ and $BeBr_2$. The data instead argue for a complex of the type $(C_6H_5)_2Be \cdot BeBr_2$. A complex is necessary, since although $BeBr_2$ forms a two-phase system in ether, the addition of $(C_6H_5)_2Be$ gives a one-phase system. The equilibrium existing in organoberyllium halides is therefore best written as

$$R_2Be + BeX_2 \rightleftharpoons R_2Be \cdot BeX_2$$

The structure of the complex is at present unknown but is probably



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[11] G. Wittig, *Ann.*, **571**, 167 (1951); **577**, 11 (1952).

[12] Reported energy of the $Be^7\gamma$ is 0.479 Mev.; "Nuclear and Radiochemistry," G. Friedlander and J. Kennedy, John Wiley and Sons, Inc., New York, N. Y., 1956.

It seems therefore that except for Hg, the group II organometal halides exist as $R_2M \cdot MX_2$ complexes rather than as RMX. The reason for this is not immediately obvious.

Further work in the Zn and Ba systems is now being conducted.

Acknowledgments.—The author wishes to thank Dr. Hershel Hausman and the staff and crew of the Ohio State University Cyclotron for the bombardment, and Dr. Byron Branson of the Robert A. Taft Sanitary Engineering Center of the U. S. Public Health Service for the use of counting equipment, and to acknowledge the financial support in the form of a Frederick G. Cottrell Grant from the Research Corporation. He also wishes to express his gratitude for stimulating conversations with Dr. George S. Handler, Tufts University.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO.]

The Electrochemical Degradation of Quaternary Ammonium Salts. II. The Mechanism of the Coupling Reaction

BY SIDNEY D. ROSS, MANUEL FINKELSTEIN AND RAYMOND C. PETERSEN

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The cathodic decomposition in N,N-dimethylacetamide or dimethylformamide of quaternary ammonium nitrates containing benzyl, fluorenyl, cinnamyl, *p*-methoxybenzyl or α-phenylethyl groups yields the coupling products of these radicals. The reaction involves the generation and dimerization of free radicals, formed in a one-electron transfer at the cathode. This is indicated by the fact that *d*-α-phenylethyltrimethylammonium nitrate gives only inactive products.

In a previous report from this Laboratory,[1] it was shown that the electrolysis of aqueous solutions of selected quaternary ammonium salts resulted in the cleavage of one of the alkyl groups attached to nitrogen to form a hydrocarbon and a tertiary amine. For one salt, benzyldimethylanilinium trifluoroacetate, the electrolyses were carried out in both water and dimethylacetamide. In water the products were toluene and dimethylaniline but, in the latter solvent, the same amine and bibenzyl were obtained. It is our present purpose to show that coupling products are generally obtained when the reaction is effected in an appropriate non-aqueous solvent of high dielectric constant and, further, to cite evidence which indicates that these reactions involve the formation and subsequent reactions of free radical intermediates at the electrode.

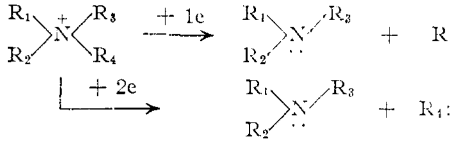
The results of six preparative experiments are summarized in Table I. The solvent in these experiments was either dimethylacetamide or dimethylformamide. No effort was made to ensure the complete decomposition of the quaternary ammonium ions in these electrolyses, and conditions for maximizing the yields were not explored. These results, therefore, have only qualitative significance and do not permit any clear decision as to the possible preparative value of this reaction.

TABLE I

CATHODIC COUPLING REACTIONS

Quaternary ammonium nitrate	Product	Yield, %
Benzyltriethylammonium	Bibenzyl	31.9
Benzyldimethylanilinium	Bibenzyl	35.0
p-Methoxybenzyltrimethylammonium	4,4′-Dimethoxybibenzyl	15.0
Cinnamyldimethylanilinium	Dicinnamyl	6.0
Fluorenyltrimethylammonium	Difluorenyl	26.1
α-Phenylethyltrimethylammonium	2,3-Diphenylbutane	30.0

The problem of mechanism for these reactions resolves itself into the question of whether the cathodic reaction involves a one-electron change and the formation of radical intermediates or, alternatively, a two-electron transfer and carbanion intermediates. The two possibilities may be formulated as



The coupling product could result either from dimerization of the radicals or a nucleophilic displacement reaction by the carbanion on the quaternary ammonium ion.[2]

Some qualitative evidence which favors the free-radical mechanism has been presented,[1] but definitive proof is lacking. An experiment with an optically active quaternary ammonium salt would permit a clear choice between the alternatives provided that the cleavage occurred at the asymmetric carbon atom and the coupled product was not formed in only the *meso* form. α-Phenylethyltrimethylammonium nitrate proved suitable for this purpose. It could be obtained optically active and gave both *meso*- and *dl*-2,3-diphenylbutane on electrolysis. In the electrochemical decomposition of active α-phenylethyltrimethylammonium nitrate, that portion of the hydrocarbon product which was not *meso* would be expected to be totally inactive, if free radicals are the intermediates. Since the radicals, if formed, are formed singly rather than in pairs, this is a more straightforward case than the decomposition of a diacyl peroxide where

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[1] M. Finkelstein, R. C. Petersen and S. D. Ross, THIS JOURNAL, **81**, 2361 (1959).

(2) Mechanisms involving hydrogen abstraction from the quaternary ammonium ion by the carbanion, $R_4:^-$, have not been considered, since the hydrocarbon R_4H was not found in the products under the present experimental conditions. Hydrogen abstraction is, in fact, a more probable reaction for these species than is displacement, and this may be considered as evidence against the carbanion mechanism.